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Thermodynamic properties, mesomorphic transitions and recycling behaviour of cholesteryl laurate using DSC technique

Jagdish Shukla*
Department of Physics, Lucknow University, Lucknow, India
and
S K Suri
Department of Physics, University of Gar Younis, Benghazi, Libya

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Structural changes arising from transition between the mesophases of liquid crystalline materials are generally studied using optical properties (Brown *et al* 1971, Brown and Shaw 1957, Coates *et al* 1972, Ennulat 1967, Gray 1962, Sackman and Dermus 1969, Sackman and Demus 1966, Saupe 1968) and/or thermal properties (Coates *et al* 1972, Ennulat 1967, Porter *et al* 1969). Sometimes the optical techniques yield ambiguous results (Coates *et al* 1972). It is therefore important to rely on other techniques and the thermal methods for detecting the phase transition involving subtle changes in the molecular order, have been found to be highly sensitive and have been widely used.

The mesomorphic states of cholesteryl laurate have been widely known from the earlier studies of Arnold *et al* (1969) and Demus and Wartenberg (1975) and his group. Since the exact nature of the change occurring in the molecular ordering when the liquid crystal is subjected to recycling was not clearly known, an attempt was made to undertake the measurements for repeated cycles and to study the effect of recycling on the thermodynamic properties, ΔH and ΔS and thus to the molecular ordering of the material.

The differential scanning calorimetry (DSC) set-up consists of a TC-10 processor, a TG 50 thermobalance and a Mettler DSC 30 low temperature cell. The purity of sample as quoted from manufacturer's data was 99%.

Differential scanning calorimetry thermograph for cholesteryl laurate for both the heating and cooling cycles have been shown in Figures 1 and 2. The phase transition temperatures, enthalpies and entropies of activation for the transition process for various cycles are given in Table 1.

*To whom the correspondence to be addressed.

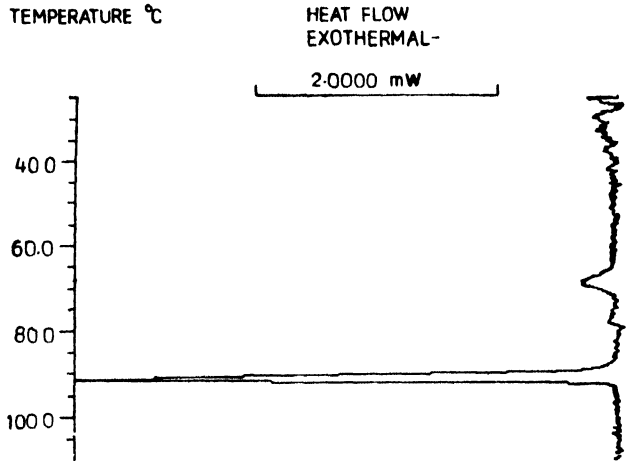

Figure 1. DSC thermogram for CH laurate on heating at 1°C min (first cycle).

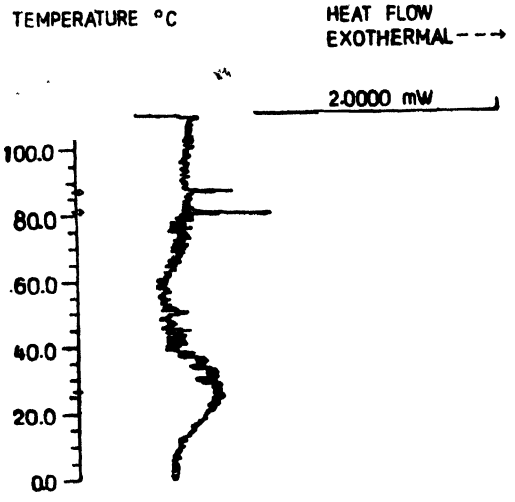

Figure 2. DSC thermogram for CH laurate on cooling at 1°C min (fourth cycle).

Cholesteryl laurate exhibited two distinct phase transition temperatures, at 341.1 K and 363.9 K respectively in the first run. The latter transition (363.9 K) compares well with the reported value of Arnold *et al* (1969) and Demus and Wartenberg (1975) respectively (364.3 K, 364.4 K) and corresponds to the solid-isotropic phase (K-Iso). The first one at 341.1 appears to be a pre-transition behaviour exhibited before the solid melts to an isotropic liquid. This could be assigned to either a glassy state or another solid to solid ($K_I - K_{II}$) transition. The transition in all other three runs exhibited similar behaviour.

In the cooling cycle, the first two runs yielded two separate phase transitions each of 361.1 K, 353.8 K and 360.8 K, 353.8 K when cooled down in the range of

100°C to 20°C and three transitions each of 360.3 K, 353.6 K and 298.9 K and 360.1 K, 353.5 K and 298 K when cooled down in the range of 110°C to 0°C. These transitions could be assigned to isotropic-cholesteric and cholesteric-smectic in the first two runs and the third transition could be due to smectic to solid crystalline phase.

Table 1. Transition enthalpies and entropies of cholesteryl laurate for different cycles.

Cycle number	Transition temperature °K	ΔH kJ mol^{-1}	ΔS J deg^{-1} mol^{-1}
Heating run			
1	341.1	4.9	14.4
	363.9	31.2	85.7
2	347.4	5.0	14.5
	363.6	29.7	81.7
3	346.2	5.7	16.4
	363.5	28.3	90.5
4	349.6	10.0	28.5
	363.3	26.8	73.7
Cooling run			
1	361.1	0.8	2.3
	353.8	1.0	2.9
2	360.8	0.9	2.6
	353.8	1.1	3.2
3	360.3	0.7	2.0
	353.6	0.8	2.4
	298.9	24.1	80.7
4	360.1	0.8	2.2
	353.5	1.3	3.8
	298.0	28 3	95.0

In the heating cycle, the enthalpies and entropies in the first two runs for corresponding transitions were 4.9, 5.0 kJ mol^{-1}, 31.3, 29.7 kJ mol^{-1} and 14.4, 14.5 J mol^{-1} deg^{-1} and 85.5, 81.7 J mol^{-1}, respectively. The ΔH of 4.9 and 5.0 kJ mol^{-1} being considerably higher than for glassy state (Ali 1985), this transition can possibly be assigned to solid-solid transition called K_I-K_{II}.

In the third and fourth cycles, the enthalpies corresponding to the first transitions were 5.7 kJ mol^{-1} and 10.0 kJ mol^{-1} and entropies 16.4 J mol^{-1} deg^{-1} and 28.5 J mol^{-1} deg^{-1}, respectively. Similarly, for solid-isotropic transition

the ΔH obtained were 28.4 kJ mol^{-1} and 26.8 kJ mol^{-1} whereas ΔS obtained were 90.5 J mol^{-1} deg^{-1} and 73.8 J mol^{-1} deg^{-1}, respectively.

It may be seen from Table 1, the enthalpies (ΔH) as well as the entropies (ΔS) for solid-solid transition increase as we proceed from the first cycle of measurement to the fourth cycle. The change in the fourth cycle is maximum for both the parameters. This shows a decrease in the molecular ordering with successive runs during the $K_I - K_{II}$ transition. On the other hand for the second transition of solid-isotropic liquid, as we proceed from the first cycle to the fourth cycle of measurement, both ΔH and ΔS reduce successively (exception of ΔS in the third run) with maximum values of ΔH (31.2 kJ mol^{-1}), and ΔS (85.8 J mol^{-1} deg^{-1}) in the first run and minimum values being 26.8 kJ mol^{-1} and 73.8 J mol^{-1} deg^{-1} respectively in the fourth run. This indicates an increased ordering in the solid-isotropic state with recycling.

In the cooling cycles, the first two runs recorded small ΔH and ΔS values, with transition temperatures of 361 K and 353 K respectively, suggesting that the molecular system does not reach the crystalline state. Further, some workers (Sackman and Demus 1966) have suggested the existence of a blue phase at about 360 K. In this laboratory (Guda 1984) also, the measurements by polarising microscope have shown the presence of blue phase at 360.5 K. However, with the DSC measurement it is not possible to distinguish between the cholesteric and blue phases in view of small difference in the enthalpy values.

The crystalline state could be achieved in the third and fourth run when cooled down to 0°C. The enthalpies obtained were 0.7 kJ mol^{-1}, 0.8 kJ mol^{-1} and 24.1 kJ mol^{-1}, entropies being 2.0 J mol^{-1} deg^{-1} and 80.7 J mol^{-1} deg^{-1}. The first two values were similar to those observed for the first and second cycles each. However, the third transition having yielded a very high enthalpy and entropy may be compared to those in the crystalline state obtained while heating the material.

Similar behaviour was observed in the fourth cycle with the third transition at 298° K yielding ΔH of 28.3 kJ mol^{-1} and ΔS of 95.0 J mol^{-1} deg^{-1} and suggesting the smectic-solid transition as in the third cycle.

In the heating cycle, the observed behaviour of the cycling on the transition temperature and thermodynamic parameters for $K_I - K_{II}$ transition indicated slight decrease in ordering from first to fourth cycle.

The second transition (K_{II}-Isotropic), however, indicates slight increase in ordering with number of cycles. In the cooling run, the third and fourth cycles which exhibit smectic-solid phase, there is an indication of slight decrease in the transition temperature and corresponding increase in ΔH from 24.1 kJ mol^{-1} to

28.3 kJ mol^{-1} and ΔS from 80.7 J mol^{-1} deg^{-1} to 95.0 J mol^{-1} deg^{-1} respectively. This again indicates that the fourth cycle was probably less ordered than the third cycle for smectic-solid phase.

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